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DETERMINATION OF CERTAIN THERMODYNAMIC PARAMETERS OF SUBSTANCES BY THE SIMILARITY PRINCIPLE

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ABSTRACT

The parameters and enthalpy-entropy state diagram are calculated for lithium in the vapor state, applying thermodynamic similarity methods. The criteria for choosing substances thermodynamically similar to lithium are discussed. To make up for the dearth of data relating to the parameters of all these substances at high temperatures and pressures in the critical region, scaling factors are calculated so that the data for better-known but thermodynamically dissimilar substances in the region of low temperatures and pressures can be extrapolated into the region of high temperatures and pressures for the lithium group. Although applied to the particular case of lithium as a heat transfer agent, the method is of interest for its applicability in general.

Author

SYMBOLS

p	pressure, newtons/meter^2
T	temperature, degrees Kelvin
V	volume, meters^2
$\pi = p/p_{cr}$	reduced pressure
$t = T/T_{cr}$	reduced temperature
$\phi = V/V_{cr}$	reduced volume
μ	molecular weight

Numbers in the margin indicate pagination in the original foreign text.

R	gas constant
i	enthalpy, kilojoules/kilogram
s	entropy, kilojoules/kilogram-degree
$\bar{i}$, $\bar{s}$	dimensionless enthalpy and entropy
k_i, k_s, k_T	enthalpy, entropy, and temperature scaling factors
cr	"critical"
hta	"Heat transfer agent"
$\bar{k}_i$, $\bar{k}_s$	scaling factors for the relative enthalpy and entropy

INTRODUCTION

The present article undertakes the rather narrowly restricted problem of calculating the parameters of wet lithium vapor in the entire region bounded by the boundary curves and the superheated vapor region joining the outer boundary curve. The method of calculation, however, is sufficiently general and well suited (by virtue of the characteristics of the experimental data for various substances) for many other heat transfer agents in regions of sufficiently high temperature and pressure.

The essence of the method is contained in the following.

The first step is to select, according to a series of criteria, a group of thermodynamically similar substances, including substances that have been subjected to thorough experimental investigation ("basis" substances), as well as substances with unknown thermodynamic parameters but of importance from the viewpoint of particular engineering applications.

The second step consists in determining the necessary critical parameters of the substances in which we are interested, in order to establish the corresponding states of the "basis" and the investigated substances.

The third step is to construct dimensionless $\bar{i}$-$\bar{s}$ diagrams for the group of thermodynamically similar substances.

The the case of lithium, the task is rather complicated if we consider 107 the interval of temperatures and pressure just below critical. This relates to the fact that, of the group of similar substances of which lithium is a member, there is not one substance whose thermodynamic properties have been studied in the required temperature and pressure intervals and that could be used as the "basis" substance. In this case, the properties are extrapolated in approximate fashion into the regions of high temperatures and pressures by the introduction of appropriate scaling factors for the dimensionless functions of thermodynamically dissimilar substances. All of these problems will be given special treatment in the present paper as part of the construction of the dimensionless $\bar{i}$-$\bar{s}$ diagram.

SELECTION OF A GROUP OF THERMODYNAMICALLY SIMILAR SUBSTANCES, WITH LITHIUM AS A MEMBER

In picking out the group of similar substances, including lithium, it should be realized that sufficient data are lacking on the law of van der Waals interaction for lithium atoms. Consequently, we cannot use the criterion of "proportionality" between the interaction energy of different substances.

A possible basis for the selection of such a group is found in viscosity data (ref. 2), which confirm the generality of the viscosity function with respect to the following liquid metals: tin, mercury, antimony, bismuth, gallium, and lithium. According to reference 2, a group of materials similar in their

viscosity is a thermodynamically similar group. In composing the group, we can also rely on the criterion of equal coefficients $RT_{cr}/p_{cr}V_{cr}$. The critical parameters of the substances in which we are interested, such as lithium and others, can be determined by using the data obtained in reference 5.

DIMENSIONLESS $\bar{i}$-$\bar{s}$ DIAGRAM FOR THE GROUP OF SIMILAR SUBSTANCES INCLUDING LITHIUM

We will construct a unified dimensionless $\bar{i}$-$\bar{s}$ diagram suitable for the entire group of thermodynamically similar substances. As the basis for such a diagram in the region of relatively low, subcritical parameters, it is convenient to use the existing experimental data for mercury (as the most exhaustively studied member of the group). Extrapolation of the dimensionless diagram into the critical region can be accomplished, for example, on the basis of the experimental data for water. To provide a comparison, the extrapolation has also been carried out on the basis of the experimental data for CO_2. This permitted us to check and improve the accuracy of several of the resultant characteristics.

For mercury and lithium on the one hand, water and CO_2 on the other, there are not states where all of the reduced parameters (π, t, ϕ) will coincide. Therefore, comparing the states in the region of interest with certain equal reduced parameters (e.g., $\pi_{Hg} = \pi_{H_2O} = \pi_{CO_2}$), we obtain different values for other parameters ($t_{Hg} \neq t_{H_2O} \neq t_{CO_2}$, etc.).

The procedure for refining the characteristics determined from the diagram 108 for Hg, H_2O, and CO_2 can be carried out by introducing appropriate scaling factors, which are determined from a comparison of the data for mercury, water, and CO_2 in comparable regions for which experimental data available for all three heat transfer agents.

To construct the $\bar{i}$-$\bar{s}$ diagrams, we introduce the dimensionless enthalpy and entropy:

$$\bar{i}_{hta} = I \cdot (1/RT_{cr})_{hta}, \qquad \bar{s}_{hta} = I \cdot (s/R)_{hta}, \tag{1}$$

$$\bar{i}_{hg} = I \cdot (1/RT_{cr})_{Hg}, \qquad \bar{s}_{Hg} = I \cdot (s/R)_{Hg}, \tag{2}$$

where

$I = 102$ (kilograms/kilojoule)

For thermodynamically similar substances (li and Hg), the expressions for the enthalpy and entropy are written

$$i_{Li} = i_{Hg} \frac{Hg}{Li} \frac{(T_{cr})_{Li}}{(T_{cr})_{Hg}},$$

$$s_{Li} = s_{Hg} \frac{Hg}{Li}, \tag{3}$$

and the scaling factors, correcting for the thermodynamic dissimilarity of the heat transfer agents - mercury, water, and CO_2 - take the following form:

enthalpy and entropy scaling factors:

$$(k_i)_{hta} = i_{hta}/i_{Hg}, \qquad (\bar{k}_i)_{hta} = \bar{i}_{hta}/\bar{i}_{Hg}, \tag{4}$$

$$(k_s)_{hta} = s_{hta}/s_{Hg}, \qquad (\bar{k}_s)_{hta} = \bar{s}_{hta}/\bar{s}_{Hg}; \tag{5}$$

temperature scaling factor:

$$(k_t)_{hta} = t_{hta}/t_{Hg}. \tag{6}$$

Making use of equations (1) to (6) and admitting certain simplifications, we obtain

$$\bar{i} = 0.01350\, i_{Hg}, \qquad \bar{s} = 24.00\, s_{Hg},$$

$$\bar{i} = 0.00334 \frac{1}{(\bar{k}_i)_{H_2O}} i_{H_2O}, \quad (7) \qquad \bar{s} = 2.16 \frac{1}{(\bar{k}_s)_{H_2O}} s_{H_2O}, \quad (8)$$

$$\bar{i} = 0.01740 \frac{1}{(\bar{k}_i)_{CO_2}} i_{CO_2}, \qquad \bar{s} = 5.32 \frac{1}{(\bar{k}_s)_{CO_2}} s_{CO_2}.$$

Some of the values of the scaling factors correcting for the thermodynamic dissimilarity of mercury, water, and CO_2 are shown in the table.

TABLE

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Scaling factors \ π	0.01	0.10	0.50	0.66	0.80
$(\bar{k}_i)_{H_2O}$	1.92	1.89	1.73	1.69	1.68
$(\bar{k}_i)_{CO_2}$	-	2.29	2.19	2.12	2.12
$(\bar{k}_s)_{H_2O}$	1.14	1.12	1.25	1.18	1.16
$(\bar{k}_s)_{CO_2}$	--	2.24	2.76	2.64	2.72
$(k_\tau)_{H_2O}$	1.60	1.59	1.64	1.57	1.55
$(k_\tau)_{CO_2}$		—	1.53	1.58	1.57

Using the results obtained, we construct a dimensionless $\bar{i}$-$\bar{s}$ diagram for the group of thermodynamically similar substances of which lithium is a member (fig. 1).

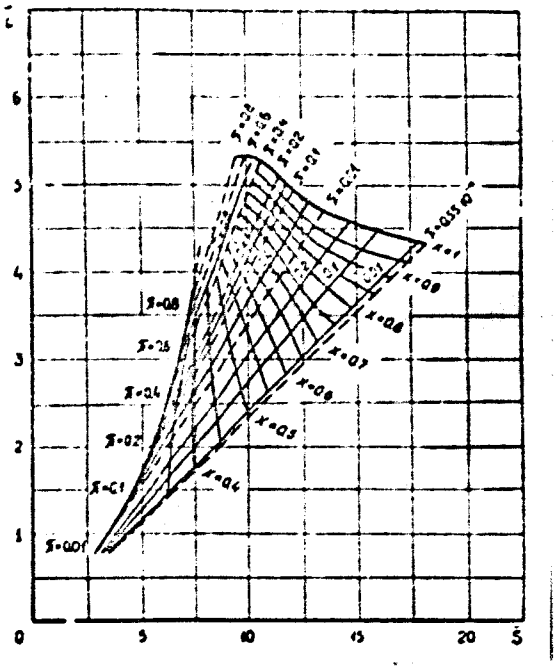

Figure 1.

From the relations (2), (7), and (8), we obtain expressions for the absolute (dimensional) enthalpy and entropy of any substance contained in the group of substances thermodynamically similar to mercury: 110

$$i_{hta} = 8.35(T_{cr}/\mu)_{hta} \cdot \bar{i},$$

$$s = 8.35\ \bar{s}/\mu_{hta}.$$

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